

# The Behavior of Cyclohexane Confined in Slit Carbon Nanopore

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## Abstract

It is well known that confining a liquid into a pore strongly alters the liquid behavior. Investigations of the effect of confinement are of great importance for many scientific and technological applications. Here we present a molecular dynamics study of the behavior of cyclohexane confined in carbon slit pores. The local structure and orientational ordering of cyclohexane molecules are investigated. It is shown that the system freezes with decreasing the pore width, and the freezing temperature of nanoconfined cyclohexane is higher than the bulk one.

**Keywords:** Cyclohexane, slit pore, graphite walls, local structure, orientational ordering, freezing. ■

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# I INTRODUCTION

It is well known that the nature of spatial ordering of a molecular system depends on the dimensionality of the space to which it is confined. Confinement can modify the dynamics, the thermodynamics and the structural properties of liquids when the range of molecular interaction and the length scale associated with position correlations in a system are similar to the length scale of confinement<sup>1</sup>. As a result, fluids confined in a pore demonstrate the behavior strongly different from the bulk case. In slit pores the melting temperature depends strongly on the pore width  $H$  and the nature of the fluid-wall and fluid-fluid attractive interaction<sup>2</sup>. The parameter  $H$  determines not only the magnitude of the shift of the melting temperature but also the structure of confined fluids and appearance of the possible new phases. The density profile becomes modulated unlike the isotropic one in bulk liquids. The study of different nanoconfined systems becomes important for both fundamental research and technology because there are a lot of real physical and biological phenomena and processes that depend on the properties of such systems. Nanoconfinement is considerably interesting also due to the new physics observed in these systems.

In spite of great importance of this issue, there is a lack of systematic investigations of effect of confinement on the behavior of aromatic hydrocarbons. Only the case of benzene received a lot of attention in the literature<sup>3–12</sup>. However, liquids with more complex chemical structure are also of interest.

In this paper, we present a systematic molecular dynamics study of cyclohexane in the slit carbon pores. In our previous publications we considered the behavior of benzene in slit pores with graphite and amorphous carbon walls<sup>11</sup> and inside an armchair nanotube<sup>12</sup>. Benzene has chemical formula  $C_6H_6$  and planar molecule. The chemical formula of cyclohexane is  $C_6H_{12}$ . Adding six more hydrogens changes the bonding inside the carbon ring and therefore alters the interaction of the ring with external molecules. Moreover, the molecule changes its shape: it is not a planar, but warped. In this respect it is interesting to compare the behavior of benzene and cyclohexane in the same kinds of pores. Three types of differences can affect the results: the different bonding inside the molecules, the different geometric shape of the molecules and the different number of hydrogens.

The planar structure of the benzene molecule corresponds to the in-plane  $sp^2$  hybrid orbitals of  $C$ , which produce a resonant bond shared by all  $C$  atoms. The cyclohexane molecule has six  $sp^3$  carbon atoms. The strong  $\pi$ -electron interaction of benzene with nanopore surfaces was found<sup>6-8,13</sup> which plays an essential role in the formation of the local structure of nanoconfined benzene<sup>11,12</sup>. At the same time the stronger cyclohexane absorption on graphite than benzene absorption was observed<sup>14</sup>, and one can suppose that the interaction of  $sp^3$  carbon atoms of cyclohexane with the graphite confining walls can lead to different structure and thermodynamic behavior of cyclohexane in comparison with benzene.

The behavior of cyclohexane in nanopores is interesting in its own rights. In particular, in Ref.<sup>15</sup> it was proposed to use cyclohexane for calibration of NMR experiments which can be important for development of experimental techniques. Several publications described the behavior of cyclohexane in mica pores<sup>16,17</sup>. For example, in Refs.<sup>18-20</sup> the crystallization of cyclohexane confined between parallel mica surfaces was studied. It was found that with decreasing the pore width up to about  $4nm$  (6 or 7 layers of cyclohexane) the crystallization occurs which is observed from the sudden increase of a yield stress. It is interesting that it was found the remarkable increase of the melting temperature in comparison with the bulk case. In experiments<sup>18-20</sup> the solidification was observed at pressures close to the atmospheric ones, which gives the possibility to suppose that the geometric confinement alone can lead to the solidlike behavior. However, in Ref.<sup>21</sup> this result was opposed, because in this work the experiment was repeated, and no evidence of the increase of melting temperature was found. The qualitative support for the results of Refs.<sup>18-20</sup> was obtained from computer simulations of model systems<sup>22,23</sup>.

An analysis of Ref.<sup>23</sup> suggests that the sign of the change of the melting temperature under confinement depends on the ratio of the fluid-wall to the fluid-fluid attractive interaction. A number of studies of different systems confined within activated carbon fibers show that the freezing temperature can increase or decrease depending on the nature of the system. In Ref.<sup>24</sup> it was found an increase about  $65K$  in the freezing temperature of benzene in activated carbons. On the other hand, for water, a considerable decrease of the freezing temperature was observed<sup>25,26</sup>.

It is interesting to note that in some cases the intermediate hexatic phase can exist<sup>23,25</sup>.

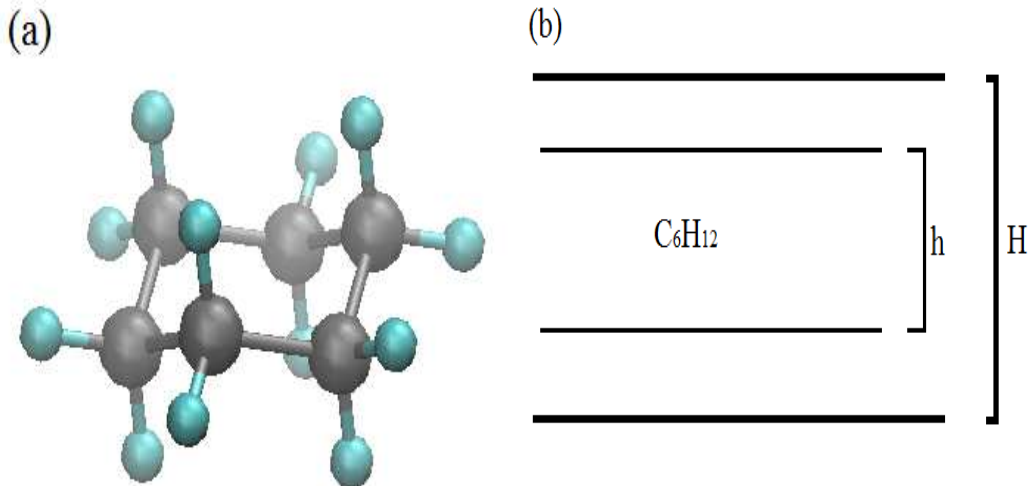


Figure 1: (a) Cyclohexane molecule. Larger balls represent carbon atoms while the smaller ones - hydrogens. (b) A cartoon of the simulation box (see the text).

As it was proposed in Ref.<sup>23</sup> the hexatic phase can be observed for the small number of layers. For example, in  $CCl_4$  the hexatic phase was found for two layers<sup>23</sup>. In the case of water the hexatic phase does exist in the case of strictly two-dimensional model<sup>27–29</sup> which demonstrates waterlike behavior<sup>30–32</sup>.

In the present paper, we study the local structure and freezing transition of system of cyclohexane molecules confined in graphite slit pores using the realistic AIREBO potential<sup>33</sup>. The molecular models and simulation methods are described in Sec. II, and the results are presented in Sec. III and discussed in Sec. IV.

## II METHODOLOGY

We start with brief description of cyclohexane molecule. It consists of a six carbon ring with two hydrogen atoms bonded to each of the ring sites (Fig. 1). Unlike benzene, the carbon ring of cyclohexane is not flat, but warped. The total size of the molecule is approximately  $5.8\text{\AA}$ .

The simulation methodology is similar to the one used in our previous publication for benzene<sup>11</sup>. We studied 200 molecules of cyclohexane in slit pores. The walls of the pores

consisted of two graphite layers. The inner layer was mobile while the outer one was held rigid in order to stabilize the system. The distance between the outer graphite layers is denoted as  $H$ . The inner layers are separated from the outer ones by  $3.4\text{\AA}$ . We denote the distance between the inner layers as  $h$ . Obviously,  $h = (H - 6.8)\text{\AA}$ . The parameter  $h$  determines the area in  $z$  direction available for cyclohexane molecules.

The system was simulated by molecular dynamics method in  $NVT$  ensemble (constant number of particles, volume and temperature). The temperature was maintained at  $T = 300\text{K}$  by means of Nose-Hoover thermostat. The timestep was  $dt_{gr} = 0.001$  fs. The system was equilibrated for  $1.5 \cdot 10^6$  steps. Then  $5.0 \cdot 10^6$  steps were done in order to calculate the averages.

In order to see the effect of the walls separation on the structure of the liquid we simulate the system at different pore heights. The system sizes in  $x$  and  $y$  direction are  $L_x = 49.1902\text{\AA}$  and  $L_y = 46.86\text{\AA}$ . The size in  $z$  direction (from the bottom of the lower wall up to the top of the upper wall) changes from  $H^{min} = 19.355\text{\AA}$  up to  $H^{max} = 33.355\text{\AA}$  with step  $dH = 2.0\text{\AA}$ . In total, 8 different pore sizes were studied.

The system was periodic in  $XY$  plane, but confined along  $z$  axis which is perpendicular to the walls.

All interactions in the system were modelled by AIREBO potential<sup>33</sup>. This potential was specially developed for simulation of hydrocarbon systems. It includes carbon-carbon, carbon-hydrogen and hydrogen-hydrogen interactions, i.e. all interactions involved in the systems under investigation.

All simulations reported in this article were done in lammmps simulation package<sup>34</sup>.

### III RESULTS

As many other liquids, cyclohexane in a slit pore forms layered structures. The number densities of carbon, hydrogen and centers of mass of the molecules in the case of different pore heights are shown in Fig. 2. One can see that in the case of small pores ( $H \leq 27.355\text{\AA}$ ) three layers are formed: two next to the lower and upper walls and one in the center, while at larger separation the peak in the center splits into two ones. It is clearly seen from the

density distribution of carbons and centers of mass. At the same time the density of hydrogen atoms looks almost flat.

Below we call the layers close to the upper and lower walls as the outer ones while the layer or two layers in the center of the pore as the inner ones.

The density distribution of the carbon atoms is very sensitive to the pore height. One can see that at the height as small as  $21.355\text{\AA}$  a shoulder on the outer peaks appears. Later on it transforms into a small subpeak. At  $H = 27.355\text{\AA}$  the inner peak splits into two subpeaks. On increasing  $H$  these subpeaks become separate peaks.

The density distribution of CM are less sensitive to the change of  $H$ . One can not see small subpeaks and splitting at  $H = 27.355\text{\AA}$ . However, one observes that the central peak splits into two well defined peaks on change from  $H = 29.355\text{\AA}$  to  $H = 33.355\text{\AA}$ .

Next we consider the orientation of the cyclohexane molecules inside the pore. It is common to characterize the orientation of molecules by second order Legendre polynomial  $P_2(\cos(\theta)) = 1.5\cos^2(\theta) - 0.5$ , where  $\theta$  is the angle between some vector which can determine the molecule orientation (for example, in the case of benzene it is the normal vector to the plane of the benzene ring) and  $z$  axis.  $P_2(\cos(\theta)) = 1$  means that the molecule is parallel to the wall, while  $P_2(\cos(\theta)) = -0.5$  corresponds to perpendicular orientation of the molecule. In our previous publication we considered benzene confined in graphite pore<sup>11</sup>. It was shown that in the case of small pores the molecules lie parallel to the walls forming a planar structure. However, it can be related to the planar shape of the benzene molecules. Unlike the case of benzene the molecules of cyclohexane are not planar, which makes the situation more complex. First of all, in the case of benzene one characterizes the orientation of the molecule by the normal vector to the benzene ring plane. The carbon ring of cyclohexane molecule is not planar so one needs to adjust the definition.

A procedure for non-planar molecules was proposed in our previous publication devoted to the benzene inside a carbon nanotube<sup>12</sup>. For the sake of completeness we give a brief description of this procedure below.

Let us denote all carbon atoms in the ring by numbers from 1 to 6 and define the vectors connecting these atoms:  $\mathbf{r}_{12}$ ,  $\mathbf{r}_{13}$  and so on. Each pair of such vectors can be used to define a plane. The normal vector to this plane can be calculated as the vector product of the

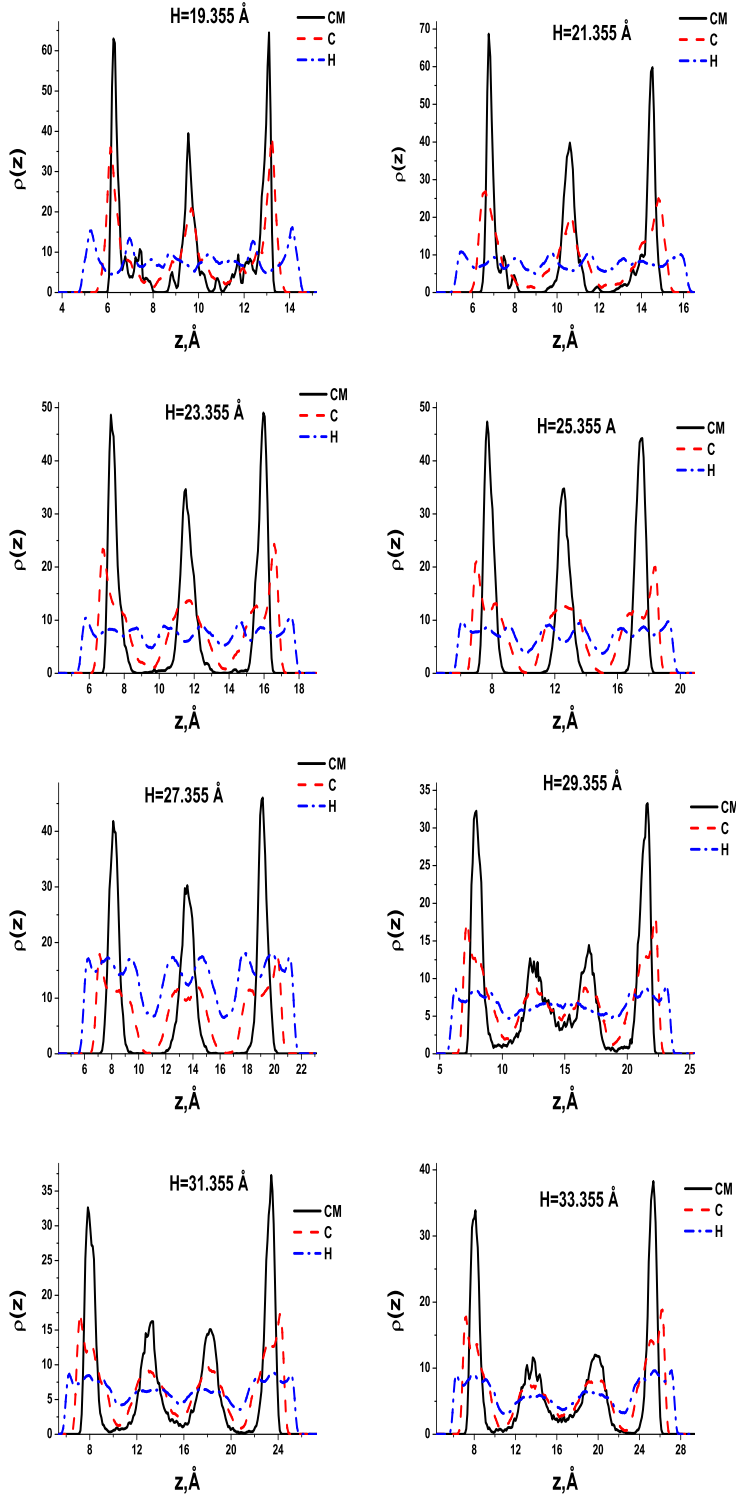


Figure 2: Distribution of number density of the molecules centers of mass (CM), carbon (C) and hydrogen (H) atoms perpendicular to the graphite wall for several pore sizes. In order to have the same scale we multiply the CM curves by 6 and divide the H curves by 2. The sizes of the pores are shown in the corresponding plots.

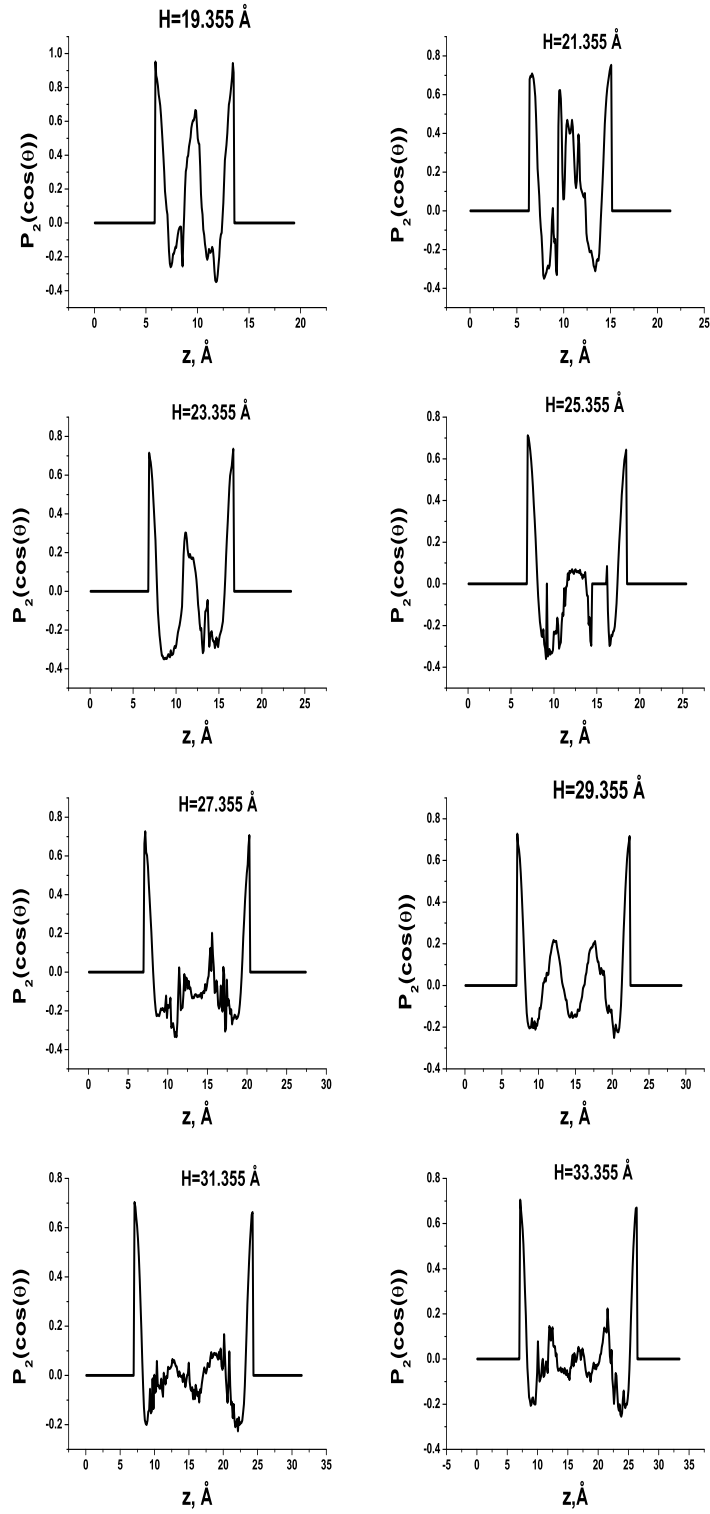


Figure 3: The distribution of second order Legendre polynomial  $P_2(\cos(\theta))$  along  $z$  axis of the system for different pore sizes.



corresponding vectors between the atoms. Employing this procedure we can calculate 20 vectors perpendicular to the planes of triplets of the carbon atoms and calculate  $P_2(\cos(\theta))$ , where  $\theta$  is the angle between the  $z$  axis and the normal vector of each plane. The final orientational parameter  $P_2$  is defined as an arithmetic average of all 20 values for different triplets.

The distributions of  $P_2$  along the  $z$  axis are shown in Figs. 3 (a)-(g). One can see that in all considered cases the molecules at the outer layers lie almost parallel to the graphite sheets. At  $H = 19.355\text{\AA}$  the corresponding peaks are almost unity. Upon increasing of  $H$  these peaks slightly decay, but even at  $H = 33.355\text{\AA}$  they are still as high as 0.7.

Unlike the outer peaks the inner one rapidly smashes out. One can see that already at  $H = 25.355\text{\AA}$  it practically disappears. Later on it splits into two peaks, but both of them are small and noisy which means that the orientational order is almost lost.

Importantly, in between of the layers the most preferable orientation of the molecules is mainly perpendicular to the wall. It means that the molecules located between the layers construct some kind of bridges between them. This phenomena can be important for stability of the layered structure.

As it was described above the system can be divided into layers. These layers can be considered as quasi two dimensional systems. This allows us to consider in-plane structure of each layer. The structure of these two-dimensional layers can be characterized by in-plane radial distribution functions  $g_2(r)$ .

In order to find the borders of the layers we took the minima of the density distribution of the centers of mass (Figs. 2). These borders are given in Table II. Note that the width of the layers can be as large as  $5 - 6\text{\AA}$ , i.e. the layers are not perfectly flat. Therefore the two-dimensional representation is not exact. However, since the width of the layer does not exceed the size of the molecules quasi two-dimensional consideration can be a useful approximate tool.

Two-dimensional radial distribution functions of centers of mass of the molecules in different layers are shown in Figs. 4 (a)-(h). The results for outer peaks of  $\rho(z)$  (Fig. ??)(curve 'wall') and for inner ones (curve 'center') are shown. For the outer peaks of  $\rho(z)$  the radial distribution function  $g_2(r)$  is averaged over the upper and the lower layers. The same aver-

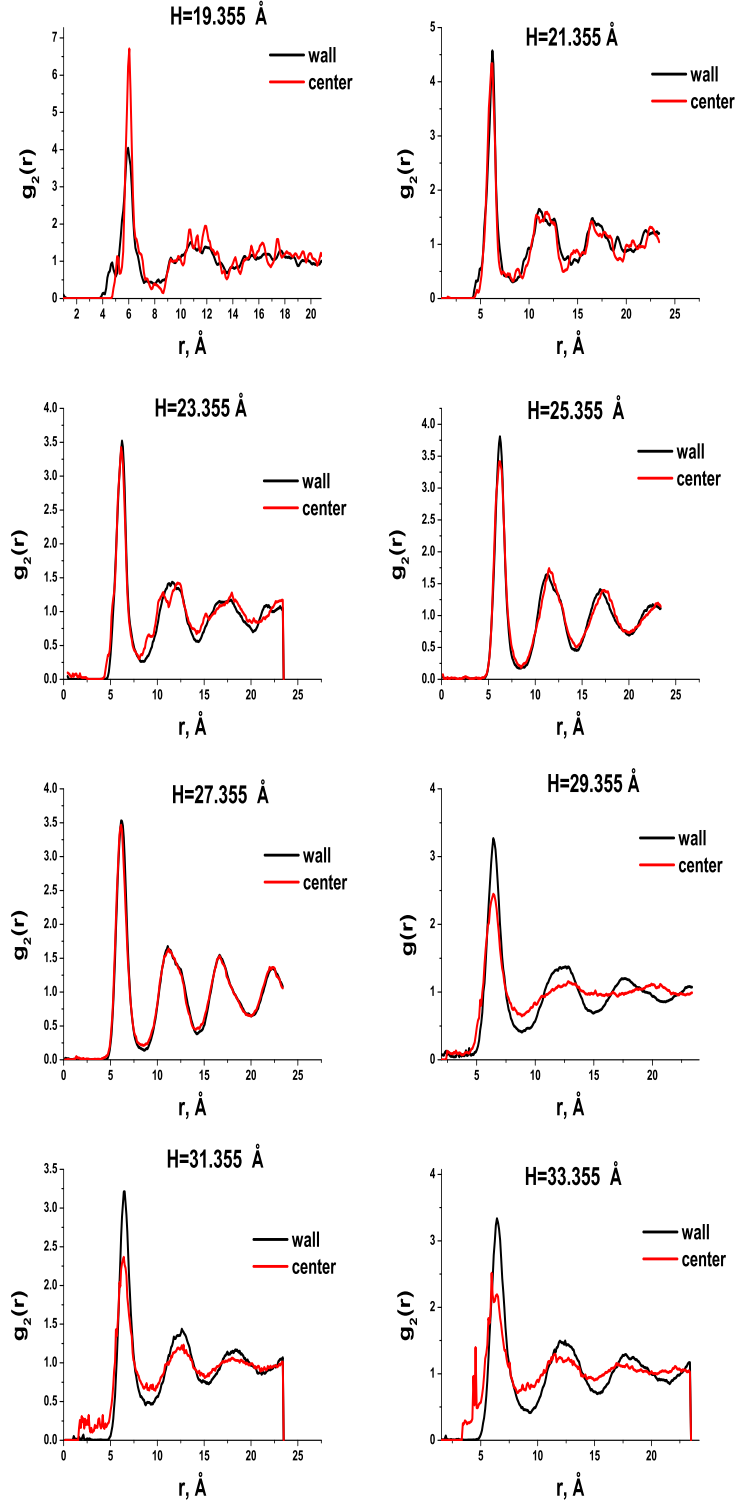


Figure 4: In-plane radial distribution functions of centers of mass of  $C_6H_{12}$  molecules in graphite pores. The data are averaged for two peaks next to the wall ('wall' curve in the plots). In the case of the peaks at the center at  $H \geq 29.355 \text{ \AA}$  the curve is averaged over two central peaks.

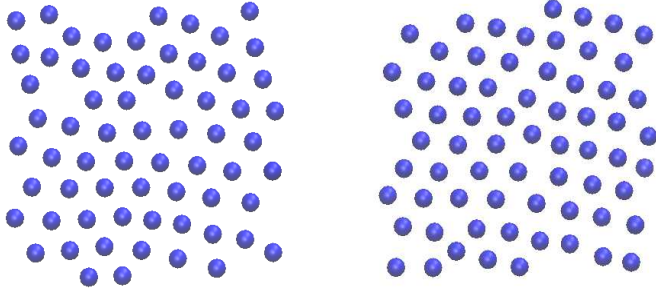


Figure 5: Left panel: Snapshot of the outer layer of centers of mass of  $C_6H_{12}$  molecules in  $H = 25.355\text{\AA}$  slit pore. Right panel: the same for the inner layer.

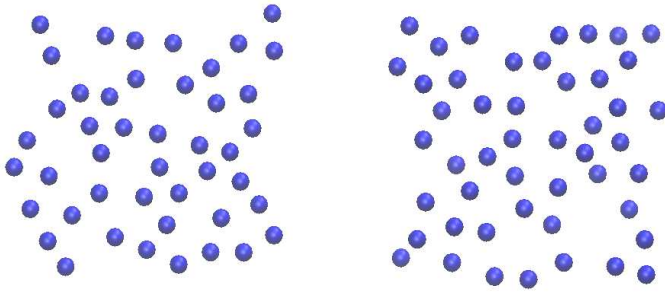


Figure 6: Left panel: Snapshot of the outer layer of centers of mass of  $C_6H_{12}$  molecules in  $H = 33.355\text{\AA}$  slit pore. Right panel: the same for the inner layer.

aging is applied to the inner layers if the central peak splits into two ones. One can see that at  $H = 19.355\text{\AA}$  the first peak of  $g_2(r)$  for the central layer is much larger than for the outer ones. We suppose that at such low walls separation the dynamics of liquid is too slow and the results strongly depend on the initial configuration. The considerable splitting of the second peak of the radial distribution function allows to suppose that in this case there is a glassy state of the system, however, more thorough investigation of this point is necessary. For  $H = 25.355\text{\AA}$  one can observe 4 peaks of  $g_2$  which corresponds to very structured liquid. Moreover the positions of the peaks is (for  $H = 25.355\text{\AA}$ )  $r_1 = 6.23\text{\AA}$ ,  $r_2 = 11.1\text{\AA}$ ,  $r_3 = 16.9\text{\AA}$  and  $r_4 = 22.26\text{\AA}$ . The ratio of  $r_2/r_1$  and  $r_3/r_1$  corresponds to hexagonal two-dimensional lattice. Fig. 5 shows a snapshot of outer layer (left panel) and inner layer (right panel) for this value of  $H$ . One can see that in both cases defected triangular lattices are formed. One can conclude from both  $g_2(r)$  for  $H = 25.355\text{\AA}$  (Fig. 4) and the snapshots of the layers (Fig. 5) that the inner and outer layers of this system are structurally equivalent.

The same conclusion holds true for the system with  $H = 27.355\text{\AA}$ . In the case of  $H = 29.355\text{\AA}$ ,  $H = 31.355\text{\AA}$ , and  $H = 33.355\text{\AA}$  the situation looks different. The crystallinity of both inner and outer layers drops. This effect is especially noticeable in the inner layers where only first peak of  $g_2$  is well pronounced, i.e. the centers of mass of the molecules in the inner layers behave as moderate density liquid.  $g_2(r)$  of outer layer looks like in the case of high density liquid. Snapshots of these cases are shown in Fig. 6.

To make the picture more clear, let us consider the behavior of the transverse  $D_z$  and longitudinal  $D_{xy}$  diffusion coefficients of the system as functions of  $H$ .  $D_z$  and  $D_{xy}$  are calculated with the help of the Einstein equation<sup>35</sup>. From Fig. 7 one can see, that for  $H \leq 27.355\text{\AA}$  diffusion coefficient becomes equal to zero. Taking into account Figs. 5 and 6, this behavior can be interpreted as the freezing transition which occurs with decreasing  $H$ . It should be noted that at  $H = 27.355\text{\AA}$  the number of layers changes from 4 to 3 (Fig. 2). It is in qualitative agreement with the experimental results<sup>18–20</sup> on the behavior of cyclohexane in mica slit pores. Moreover, in our case the freezing temperature is  $T = 300K$  whereas the bulk freezing temperature of cyclohexane is equal to  $T_b = 279.62K$ . This increase of freezing temperature is again in qualitative agreement with the experiment<sup>18–20</sup> and computer simulations of model systems<sup>22,23</sup>.

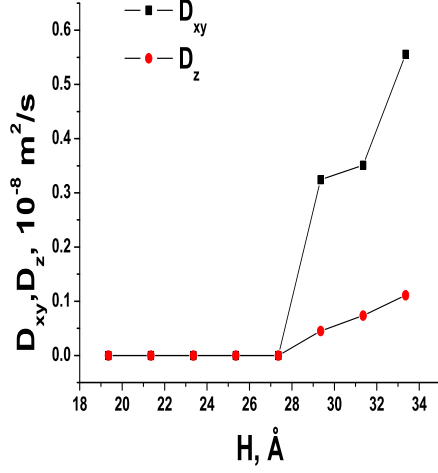


Figure 7: Transverse  $D_z$  and longitudinal  $D_{xy}$  diffusion coefficients of the system as functions of  $H$  at  $T = 300K$ .

$H, \text{ \AA}$	$h, \text{ \AA}$	$\rho, g/cm^3$
17.172	10.462	1.075
18.172	11.462	0.982
19.172	12.462	0.903
20.172	13.462	0.836
21.172	14.462	0.778
22.172	15.462	0.728

Table 1: The size of the graphite pore  $H$ , the distance between the inner graphite sheets  $h$  and the density of confined benzene  $\rho$

H	Layer 1	Layer2	Layer 3
$H = 17.172$	$z_1 = 5.29$ $z_2 = 6.49$	$z_1 = 7.97$ $z_2 = 9.17$	$z_1 = 10.68$ $z_2 = 11.71$
$H = 18.172$	$z_1 = 5.34$ $z_2 = 6.61$	$z_1 = 8.21$ $z_2 = 9.7$	$z_1 = 11.19$ $z_2 = 12.68$
$H = 19.172$	$z_1 = 5.71$ $z_2 = 7.01$	$z_1 = 8.78$ $z_2 = 10.47$	$z_1 = 11.69$ $z_2 = 13.61$
$H = 20.172$	$z_1 = 5.77$ $z_2 = 7.63$	$z_1 = 8.96$ $z_2 = 11.09$	$z_1 = 12.43$ $z_2 = 14.48$
$H = 21.172$	$z_1 = 5.25$ $z_2 = 9.14$	$z_1 = 9.14$ $z_2 = 12.03$	$z_1 = 12.03$ $z_2 = 15.16$
$H = 22.172$	$z_1 = 4.74$ $z_2 = 9.13$	$z_1 = 9.13$ $z_2 = 12.90$	$z_1 = 12.90$ $z_2 = 16.81$

Table 2: The coordinates of the borders of benzene layers for different graphite pore size.

## IV CONCLUSIONS

In conclusion, we present the molecular simulation study in NVT ensemble of the cyclohexane confined between the carbon plates (see Fig. 1) using the realistic AIREBO potential. The local structure of the system is studied as a function of the distance between the plates  $H$  and it is shown that the molecules form the layered structure. The number of layers increases with increasing the width of the pore. The orientation of the cyclohexane molecules is also studied. It is found that the molecules at the outer layers lie almost parallel to the graphite sheets, while in between of the layers the most preferable orientation of the molecules is mainly perpendicular to the wall. This behavior is similar to the one of the benzene molecules in carbon nanotubes<sup>12</sup>.

In our previous publication<sup>11</sup> we considered benzene molecules in the same kind of graphite slit pores. It was shown that at small  $H$  the outer benzene layers crystallize in a planar structure while the inner one stays relatively disordered. Unlike this, all layers of cyclohexane behave qualitatively similar: all layers simultaneously demonstrate freezing or

melting transitions. However, at large pore sizes  $H$  the outer layers become more ordered what is intuitively clear: the presence of a crystalline wall with the same symmetry as the carbon ring of cyclohexane acts as a periodic external potential on the liquid and makes it more ordered.

From the local structure (Figs. 5 and 6) and behavior of the diffusion coefficient (Fig. 7) one can conclude that the system freezes with decreasing the width of the pore and corresponding change of the number of layers from 4 to 3. It is interesting that the freezing temperature of the confined cyclohexane is higher than the bulk freezing temperature in qualitative agreement with the experiment<sup>18–20</sup> on cyclohexane confined in the mica pores. It should be noted that no signs of the hexatic phase were found in the present study, however, further investigations in this direction are necessary.

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